Cover Page

Scalable Methods for Electronic Excitations and Optical Responses of Nanostructures: Mathematics to Algorithms to Observables

A Theory, Modeling and Simulation in Nanoscience Proposal
For the period of FY03 - FY08

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Scalable methods for electronic excitations and optical responses of nanostructures: mathematics to algorithms to observables

Table of Contents

Scalable methods for electronic excitations and optical responses of nanostructures: mathematics to algorithms to observables

Abstract

Electronic and other elementary excitations play a central role in understanding and controlling the properties of nanostructures. Yet at present simulation methods are inadequate to describe these properties, being limited to either relatively small molecules or unit cells. In this proposal, theoretical methods to treat elementary excitations will be developed that merge molecular and solid state methods to address the special challenges of large disordered nanostructures. This work will adapt molecular methods to treat large numbers of particles, and solid state methods to treat systems with disorder, and combine each with embedding methods that treat extended environmental effects. Underlying all of these simulation methods are common mathematical kernels from numerical linear algebra and optimization theory that will be addressed by close interactions between simulation scientists and mathematicians. Furthermore, the problem of extending methods that describe electronic excitations to nanostructures is fundamentally one of treating electronic interactions of differing strength at different levels of resolution. This is accomplished by physical approximations above, but is essentially a more fundamental challenge. Thus, an additional central element of the proposal is close interaction between physical scientists and mathematicians to develop new multiresolution approaches to describing the behavior of electrons in nanomaterials. The work described here will specifically advance modeling of optical response, charge transport, coupling between radiation and nanomotion in nanostructures of all kinds, as well as providing broader impacts from the improvements in electronic structure simulation methodology and fundamental algorithms in applied mathematics.

Scalable methods for electronic excitations and optical responses of nanostructures: mathematics to algorithms to observables

1. Background and significance.

There has been much recent progress in the synthesis, characterization and theoretical studies of various nanostructures such as nanotubes, nanocrystals, atomic wires, organic and biological nanostructures, and molecular junctions. However, there remain immense challenges in both the basic and practical understanding of the properties of these structures and their interactions with external probes to realize the tremendous potential for application of nanostructures. Some of the most exciting frontiers in nanoscience include molecular electronics, nanoscale opto-electronic devices, nanomechanics (nanomotors), light harvesting and emitting nanostructures, among others. In all of these areas, the electronic excited properties of the nanostructures and how they are coupled to the external stimulations/probes are crucial issues. For example, in the case of a nanomotor, creation of mechanical motion (i.e., conformation changes on demand) in a nanostructure may only be achieved easily through excitations such as absorption of photon or charge transfer by physical or chemical means because of their size.

The electronic excitations and optical response in nanostructures are therefore of fundamental and technological importance.   However, these processes can be significantly different from those in the regimes of the bulk or atomic/molecular limits. Quantum confinement effects and many-electron interaction effects are known to be important (and can even be dominant) in reduced dimensional systems and can be sensitive to the exact geometric structure owing to symmetry constraints and/or the nature of the nanointerface.   In this proposal, we will initiate a program on the theory and modeling of the electronic excited-state and optical properties of various nanostructures. Our general goals are to attack existing bottlenecks in simulating excitations and optical responses of nanostructures, to seek novel reformulations of the underlying physical theories by exploring new ideas in applied mathematics, and to apply the methodology to targeted problems in nanoscience. We will develop and use a range of theoretical techniques to address the issues of electron-electron interactions, geometric constraints and reduced dimensionality, and interactions with the external environment. Since nanostructures are neither at the molecular nor the bulk limits, new mathematical and algorithmic tools will need to be developed to address the above issues.

2. Preliminary studies.

There is already a rich set of theoretical and simulation methods to draw from, and we shall illustrate some of the scientific challenges and the interactions we anticipate in the context of simulating electronic excitations. In this area, we have expertise in condensed matter approaches such as the GW/Bethe-Salpeter method, as well as molecular approaches such as time-dependent density functional theory and many-body coupled cluster theory. These methods for electronic excitations are all subject to computational bottlenecks that are far more severe than those affecting the more standard calculation of the ground state energy. Linear scaling methodologies, for example, do not yet apply to any of these approaches. Rather, the computational costs of all of these methods scale with a nonlinear power of the number of atoms, ranging from the third power (TDDFT), upwards. Current bottlenecks include construction and assembly of matrices and matrix-vector products, dense linear algebra associated with matrix diagonalization (symmetric and non-symmetric) and manipulation, solution of large linear and nonlinear systems, and large-scale optimization methods.

Another approach is to develop approximations to the above high-level calculations so they can be applied to larger systems. This approach is based on constructing the single particle Hamiltonian of a nanostructure non-selfconsistently, then solving only a small portion of its eigenstates pertinent to the optical excitation. These methods provide fast linear scaling, making them applicable to thousands or even millions of atoms, while having a direct connection to the high-level methods. By linking the selfconsistent approaches with this new approach, we can solve nanosystems of larger size with greater accuracy.

All of these existing bottlenecks form the first area of collaboration with mathematics. A second level of interaction involves consideration of the way the existing kernels are formulated. For example, multigrid ideas could impact matrix assembly in the GW method, and the present-day dense linear algebra can be reformulated into sparse linear algebra and generalized eigenvalue problems in the case of TDDFT. We shall also seek a deeper level of integration by creating smaller focused teams in which members work closely to attempt more fundamental reformulations of the physical theories to exploit recent advances in applied mathematics. For example, because electronic excitations tend to be non-local in character, it may be natural to seek multiresolution approaches to more efficiently represent the solutions. One approach for the mathematical treatment of these multiscale problems is based on the optimal prediction methodology developed by Chorin and his colleagues. In optimal prediction, we evolve a limited number of unknowns conditioned by the statistical behavior of unresolved degrees of freedom. This work, which has been successfully applied to a number of problems, provides a mathematical framework for coupling across scales. We also observe that while we have begun from a relatively specific area of nanoscience, we finish up with progressively more general questions at the level of mathematical formulations, which we believe will have potentially broader impacts on simulations in nanoscience.

3. Research design and methods.

The research issues and objectives are discussed in this section, organized in three sub-sections. The first consists of target applications in the nanosciences, on which the physical scientists will interact by bringing complementary methods and backgrounds to bear on common problems. These problems also represent challenges for simulation methods that require advances such as those described below. The second part is a discussion of plans to improve a set of four complementary physical simulation methods for describing elementary excitations in nanoscale systems. The third part is then a discussion of several common areas in applied mathematics where advances will be sought to impact the bottlenecks and issues identified in the simulation methods.

3.1 Elementary excitations and physical phenomena in nanoscale systems

The below topics cover several exciting areas in nanostructure science and applications. Although they are diverse physical phenomena, they share a common theme of involving excited state electronic structures. Quantum transport depends on electronic states near the band edge, and electron-electron interactions between these states. Optical properties are the result of electronic transitions between the ground state and the excited states. The optical-nanomechanical properties are a result of differences between the potential energy surfaces of ground and excited states. The Kondo resonances are a delicate coupling between local excited states and continuum electrons. In this proposal, we plan to develop a range of different simulation methods to address this common challenge of excited state electronic structures, and the mathematical problems that underlie such methods.

Quantum transport and tunneling through nanostructures. One of the major areas in nanoscience is molecular electronics. This field is driven by the ultimate goal of fabricating electronic devices with novel properties at the nanoscale, replacing conventional microelectronics. Such future molecular electronic devices are likely to be composed of components such as atomic wires, nanotube junctions, or molecular junctions (i.e., a single molecule attached to two leads). Calculating the electrical transport through these nanoscale objects is a major challenge because it is dominated by quantum and many-body interaction effects such as those due to electron-electron and electron-phonon interactions. An accurate determination of the quasiparticle excitation energies in such systems is a crucial first step in understanding their transport and tunneling properties. To simulate real devices, one needs to go beyond linear response and calculate the current-voltage characteristics at finite bias. This second step requires a self-consistent theory for situations with finite current and open boundary conditions, calculation of forces in the nonequilibrium state, coupling of the current to the vibrational modes and other excitations, and determination of the behavior of noises.

Photoemission and optical properties of nanostructures. The photoemission and optical properties of nanostructures are significantly altered compared to equivalent bulk systems owing to quantum confinement and enhanced Coulomb interaction effects. For example, the optical response (e.g., the color of the luminescence light) of a semiconductor nanocrystal is a sensitive function of its size, which can be tuned for different applications, and that of a carbon nanotube is also sensitively dependent on its diameter and chirality. These changes form the basis for many existing and potential optoelectronic applications of nanostructures. In this project, we plan to investigate the photoemission and optical properties of several key nanoscale systems (including nanotubes, nanocrystals, self-assembled quantum dots, and quantum wires on surface steps) by treating the many-electron interactions at the state-of-the-art level using the various techniques described in this proposal.

Excitations and nanomechanical properties. Another exciting development is the use of induced structural changes in nanostructures for mechanical applications, for example, employing them as nanomotors. Owing to the nanoscale dimensions of these structures, such applications involve, in general, conformation transformation

of the system after electronic excitation by either photon or charge injection. Understanding these phenomena requires knowing the forces on the atoms in the excited state, going beyond standard ground-state theories. Recent theoretical advances have made possible first-principles computation of such excited-state forces. We plan to apply these methods to address previously computationally inaccessible questions regarding photo-induced conformation changes, luminescence spectra, molecular dynamics in the excited state, and the microscopic structure of photo-induced defects in nanostructures.

Kondo resonances on surfaces: Another fascinating example of nanoscale phenomena is the coupling between excited states of a transition metal atom impurity and conduction levels of a metallic surface—known as the Kondo effect. While extensively studied by model Hamiltonian methods, there is an opportunity to apply many body methods for the transition metal plus local surface atoms together with embedding methods for the conduction electrons to compare directly against recent STM experiments for Co/Cu(111). This is another challenging example of the transformation of excited states from the free atom to the nanostructure environment, which could be extended to study more general perturbations of excited states of nanoclusters on surfaces or attached to leads.

3.2 Advances in simulation methods for elementary excitations

3.2.A. Many-body coupled cluster methods for excitations.

Coupled cluster (CC) theory provides an accurate and extensible approach to approximating the time-independent or time-dependent Schrödinger equation [1,2,3]. This yields the energy of ground states, and also excited states, ionized states and electron-attached states. Extensibility is obtained by truncating the cluster expansion of the wavefunction:

$$|\Psi\rangle = \exp\left(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ... + \hat{T}_n\right)|\Phi\rangle \tag{1}$$

at either single and double excitations (SD) or also including triples (SDT), etc. The accuracy of CC approaches for ground states, as well as excited state energies and properties is well-established for molecular problems. The principal difficulty is that even at the lowest level (CCSD), the number of unknowns scales as $O(M^4)$, where M is the molecule size, and evaluation of the intermediates defining the equations scales as $O(M^6)$. This limits the largest reported CCSD calculations for the ground state to systems of roughly 20 atoms or so in practice. Extension to CCSDT yields $O(M^6)$ unknowns and $O(M^8)$ scaling, while CCSDTQ is $O(M^8)$ unknowns and $O(M^{10})$ computation. In principle, this scaling problem can be ameliorated by the use of "local correlation" approximations [4], which keep only a very small fraction (perhaps asymptotically only $O(M^1)$ [5]) of the amplitudes as explicit variables. This is possible while still retaining 90% to 99% of the correct result because electron correlation is dominated by short-range interactions. Local correlation methods for ground state coupled cluster theory are under active development by various groups, including Head-Gordon's under DOE's SciDAC support, *but the approximations and algorithms are not yet mature.* Work on extension of local correlation ideas to excited states is just starting to be reported [6,7].

The objective of this part of the proposal is to make advances in CC theory and algorithms so that the power and accuracy of CC methods can be applied to nanoscience problems involving elementary excitations. This will be on the basis of progress on several inter-related fronts. The first front is development of new ideas for local CC theory for ground and excited states as laid out in this section of the proposal. The second front is attacking the bottlenecks that arise in this new approach in active collaboration with applied mathematicians. A third front is bootstrapping CC methods to still larger systems by utilizing the patching and embedding ideas discussed later in this section, in collaboration with the physical and computer scientists working on those approaches. Finally, we shall work on attempting to design true multiresolution approaches to CC theory, as discussed in the multiresolution section.

As a preliminary to discussing new approaches to excited state local correlation, we briefly review the general formalism for obtaining ground and excited state energies in CC theory. The ground state energy follows after solving non-linear equations for the cluster amplitudes contained in the substitution operators:

$$\left\langle \Phi_s \left| \hat{H} \right| \exp\left(\hat{T}_1 + \hat{T}_2 + ... \right) \Phi \right\rangle_C = 0 \qquad (2)$$

The number of projection equations is taken as equal to the number of unknowns—for example the substitutions s run over all singles and doubles in CCSD. These equations can be written terms of known matrix elements of the Hamiltonian, and unknown amplitudes that are defined by the solution of the non-linear equations. After solutions are obtained for the ground state, excited states can be evaluated by linear response theory. One looks for poles in the first-order time-dependent response of the ground state to a small time-dependent field, as a function of the applied frequency, ω. The resulting equations may be written in terms of response operators for each pole, which are the eigenvectors of a non-Hermitian eigenvalue problem of the following form:

$$\left\langle \Phi_s \left| \hat{H} \right| \left(\hat{U}_1 + \hat{U}_2 + ... \right) \exp\left(\hat{T}_1 + \hat{T}_2 + ... \right) \Phi \right\rangle_C = \omega u_s \qquad (3)$$

The cost of an iteration of the eigenvalue problem for the excited states scales exactly the same way (per state) as the cost of an iteration of the non-linear equations for the ground state.

The first step in our plan is to generalize our current local correlation ideas for ground states, to excited states. In brief summary, a local model or ansatz is introduced for the cluster operators contained in the above equations. The simplest form for this operator for the doubles (T_2) reduces their number from $O(M^4)$ to $O(M^1)$, while retaining all single substitutions in T_1. We express the correlation operator in a localized atom-centered representation using a redundant "minimal" atomic orbital basis for the occupied functions [8], and projected atomic orbitals for the empty (virtual) functions. The simplest local correlation model, "atoms-in-molecules" (AIM) keeps all correlation amplitudes that are localized entirely on a single atom, while all correlation amplitudes coupling together two or more atoms are discarded. This model is manifestly exact for an isolated atom (or an ensemble of isolated atoms), and is the strongest local correlation model that is sensible. In this approximation, the doubles pair correlation operator takes the form:

$$\hat{T}_{AIM} = \sum_{A}^{atoms} \left\{ \sum_{i \in A}^{occ} \sum_{j \in A}^{occ} \sum_{a \in A}^{virt} \sum_{b \in A}^{virt} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i \right\} \qquad (4)$$

Roughly, 85 to 90% of the correlation energy is recovered in this model for molecular ground states, based on pilot calculations [9]. The first specific objective is to implement and test this method for electronic excited states for the first time, starting at the singles and doubles (SD) level. In other words, the above equations for excitation energies will be developed with this AIM ansatz, starting at the doubles level. The prefactor of this local correlation model increases but the overall scaling (potentially *linear scaling*) is unchanged if we extend the correlation treatment from doubles to triples (or even higher). If successful, this project will offer the possibility of applicability to systems on the nanoscale, and will complement the Green's function and TDDFT approaches described in subsequent sections. Extensions to models that retain a quadratic number of amplitudes are possible, but we hope to pursue an alternative approach to refinements based on perturbation theory, discussed below.

The problem of developing effective algorithms for this problem will benefit greatly from close interactions with the math team associated with this proposal. For the ground state, we must solve linear equations that involve ill-conditioning that is a consequence of the local correlation ansatz. Additionally there is a non-linear orbital optimization problem (for the redundant localized occupied orbitals) that appears to require either generalizations

or alternatives to the usual DIIS approach. For the excited states, we then require an iterative algorithm to obtain a finite number of eigenvalues of a non-symmetric response matrix that inherits the ill-conditioning inherent in its ground state reference. Efficient algorithms for these key steps link directly with the later sections on numerical linear algebra and optimization.

Returning to the development of CC methods for excited states of nanoscale systems, we envisage a second very general step beyond this initial plan. This is to develop a new *perturbation-based* approach to correcting a reference ground state CC wavefunction that has been restricted by a local correlation model, either as discussed above, or perhaps by even stronger approximations that work in only the valence space [10]. We build upon ideas that we have developed for ground states [11,12] , as well as an approach that has previously been used without local correlation to define useful approximate CC methods for excited states [13]. In combination with local correlation, it becomes a powerful and general framework for correcting a locally correlated reference for non-local effects in the ground and excited states. For ground states, this will yield partitioned equations that self-consistently couple the locally correlated reference to neglected (nonlocal and higher) excitations, generalizing our earlier work on (2) corrections. For excited states it represents an extension of (2) that generalizes and substantially improves earlier efforts in this direction [14]. This requires substantial development and testing, but provides a framework for systematically improving the initial local correlation model. It is this ability to systematically improve the results that remains the strength of the many body coupled cluster approach.

After initial development of a pilot code and testing on toy problems to establish the minimal number of local correlation amplitudes that must be treated to all orders, we must then turn to seeking an efficient implementation of the perturbative corrections. This is because without discarding numerically insignificant terms they will scale as no better than $O(M^4)$ at the level of double substitutions, and will generally be higher for triples. We shall attempt to do this via screening without approximation in order to reduce the scaling towards linear. We shall first investigate a Laplace transform approach [15], combined with multipole treatments of well-separated interactions [16]. It is even possible to apply a more conservative local correlation model (such as one that keeps a quadratic number of amplitudes) to the weaker, more non-local interactions that being treated by the perturbative approximation.

Finally, we observe that local models of the type discussed above are essentially physically motivated multiresolution descriptions of electron correlation. The simplest AIM model merely discards all terms that are not included in the atomic ansatz (2 levels of resolution). The perturbative corrections discussed above generalize this to 3 (or maybe more) levels, by treating distant interactions by perturbation theory, as well as discarding negligible terms. We shall interact with the developers of the patching and embedding methods to extend this to an additional lower level of resolution, provided by an embedding potential from a lower level method. More fundamentally, as discussed later, we shall also work with the math team to explore whether or not it is possible to develop alternative and entirely new approaches to treating electron correlation at multiple levels of resolution.

3.2.B. The GW/Bethe-Salpeter Approach.

One of the most powerful first-principles approaches for treating excited states and addressing the above issues is the many-body Green's function method. In this approach, correlation functions (the Green's functions and closely related quantities) are calculated using perturbation theory in the screened electron-electron interaction. An advantage of the method is that the resulting correlation functions are directly related to the response functions measured in various experiments: for example, absorption coefficients, scattering cross-sections, etc. Although the many-body Green's function formalism has been around for decades [17,18], quantitative calculations based on the technique have only existed for about fifteen years [19] and are currently applied to systems containing up to tens of atoms per unit or super cell. The use of the screened Coulomb interaction has made these calculations feasible and highly accurate [19]. For example, calculations of quasiparticle self-energies have yielded accurate band-gaps of semiconductors and insulators [20].

Even though the input to the quasiparticle calculation are the one-electron states from independent-particle theories like LDA, calculations of the Green's functions, screened interactions, and self-energies, scale as a high power of the number of atoms in the system. Over the past few years, quantitative first-principles calculations of optical and UV absorption have been achieved by solving the Bethe-Salpeter equation (BSE) for the electron-hole interactions [21-23]. These calculations are computationally demanding due to the presence of excitonic correlation effects. Nevertheless, tremendous progress has been made in the past three years, in both theoretical understanding and computational methods. Successful applications of the new methods have been made to various systems including crystals, surfaces, polymers, molecules, and nanostructures.

The computational complexity of many-body Green's function calculations arises largely from the computation of multi-variable functions required for the description of many-body interactions. For example, single-particle theories (like the LDA) deal only with the one electron potential V(r), i.e., the interaction between a single electron and the surrounding mean field. Quasiparticle theories require the determination of the non-local energy-dependent electron self-energy $\Sigma(r, r',\omega)$ [19] and the solution of a Dyson's equation, in which the self-energy Σ replaces the exchange correlation potential of the LDA:

$$\left[-\frac{1}{2}\nabla^2 + V_{ion}(r) + V_H(r)\right]\psi_{nk}(r) + \int \Sigma(r, r', E_{nk})\psi_{nk}(r')\, dr' = E_{nk}\psi_{nk}(r) \qquad (5)$$

Further, to calculate optical responses such as the absorption spectrum, it is necessary to include the particle-hole interaction. This can be done properly with the BSE [21], the input to which is the particle-hole interaction kernel $K(\mathbf{r_1, r_2, r_3, r_4}, \omega)$, a four-point, energy dependent function. Once these quantities are determined, it is still necessary to solve the following matrix equation to determine the excited states and energies, whose solutions are then used to compute spectra:

$$(E_c^{QP} - E_v^{QP})\, A_{vc}^S + \sum_{v'c'} <vc\,|\,K^{eh}\,|\,v'c'>\, A_{v'c'}^S = \Omega^S A_{vc}^S \qquad (6)$$

Here v and c denote the occupied and unoccupied states. The dimension of this non-Hermitian, nonsparse matrix eigenvalue problem, typically in the order of tens to hundreds of thousands, is generally much larger than that for the independent-electron problem. To study a wide range of nanostructures, it will therefore be necessary to develop new algorithms to carry out these calculations on a scalable parallel computational environment. Moreover, in the calculation of forces in the excited state [24], we need to take derivatives of the excitation energy with respect to the atomic positions. Calculation of the derivatives of the particle-hole kernel is especially time challenging.

Thus, although considerable advance has been made in the past decade in this area, in order to accomplish the above goals for nanostructures, progress will still have to be made on a number of key scientific and computational issues. On the scientific front, it is necessary to understand better inelastic effects such as quasiparticle lifetimes [25]. The finite lifetime of excited electrons and holes contributes to the lineshape in photoemission and absorption spectra, while knowledge of the principal decay channels is necessary for the interpretation of spectroscopies involving intermediate states. Many phenomena such as bandgap renormalization in intensively excited semiconductors are related to self energy effects of quasiparticles in nonequilibrium distributions, which need to be treated by extending the standard GW approach to a nonequilibrium Green's function formalism such as the Keldysh formalism. Finally, although the calculation of forces in the excited state is now possible within the Bethe-Salpeter equation methodology, significant improvement is still needed to make these calculations feasible for large-scale applications.

Another unresolved issue is the application of the Green's function approach at the level of the GW/BSE approximation to d- and f-electron systems: many materials of current interest such as magnetic nanoparticles

involve elements with d- and f-electron outer shells. The localized nature of these orbitals can give rise to strong electron-electron correlations. Inclusion of d- or f-electrons will involve the development of more efficient algorithms to deal with the localization of these orbitals, and may also require improvements in the description of the screened electron-electron interaction. This issue is very much related to the main challenge of enhanced electron-electron correlations in reduced dimensional systems, which is a major factor in the excitation spectra and transport properties of quantum dots, atomic wires, nanotubes and other nanostructures.

3.2.C. Time-dependent density functional theory.

Density functional theory (DFT) is a highly successful theory for the electronic structure of condensed matter [26]. While DFT is exact in principle, it is commonly implemented within the local density approximation (LDA) [27], and its generalizations like the generalized gradient approximation (GGA) [28], or via some hybrid form [29]. DFT can be used to predict the ground-state properties of realistic systems, systems far larger and more complex than can be treated by other many-body methods. The unprecedented success of the DFT has opened up new avenues and applications such as predicting the structural properties of complex condensed matter systems. Specifically, new phenomena and materials properties have been predicted using DFT [30,31].

Unfortunately, the past successes of DFT have largely been limited to ground state properties, for which DFT was constructed. For example, the application of LDA (or GGA) to estimate the band gap of insulators typically underestimates the band gap by a factor of two, or more [32]. If ground state versions of LDA or GGA functionals could be applied with a similar success to excited state phenomena, then *one* theoretical framework would be available for accessing *both ground state and excited state properties*. Some progress has been made along these lines. For example, a natural and straightforward extension of DFT is to include explicit time dependence for the external potential (or probing field). This extension is known as time-dependent density functional theory, or time dependent local density approximation (TDLDA), if LDA is used. In this section, we will focus on TDLDA, but other forms could equally well be used such as GGA.

TDLDA can treat the problem of electron excitations using ground state -orbitals and energy levels as input. The theory is based a functional of the total electron density, expressed in terms of occupied one-electron orbitals [33-40]. In the presence of light, or other time-dependent external potentials, the one-electron orbitals evolve as governed by a time-dependent one-electron Schrödinger-like equation. By examining the evolution of these orbitals, one can determine the interaction of the external field and the system of interest. The validity of TDLDA in these situations can be justified via an adiabatic continuation of the ground state LDA [33]. This is the only additional approximation made within TDLDA; however, it has not been justified, except *a posteriori* [33-40].

There are two commonly used computational approaches to deriving the excited state properties using TDLDA or related methods [33-40]. One is a direct computation of the time evolution of the ground state orbitals in the presence of an external field [35]. This approach is termed the "real time" implementation of TDLDA. The orbitals satisfy a time-dependent Schrödinger equation of the form:

$$i\frac{\partial \phi_i}{\partial t} = H(t)\phi_i(t) \qquad (7)$$

with some initial conditions, where H(t) is the time-dependent Hamiltonian and $\phi_i(t)$ are the occupied Kohn-Sham orbitals. In standard approaches, each of these orbitals is integrated over a certain interval of time. The resulting orbitals are then used to extract physical quantities, such as the time-dependent induced dipole: $z(t) = \int \phi_i^* z \, \phi_i \, d^3r$. The power spectrum of this dipole is a measure of the optical absorption of the system.

Another approach is based on linear response theory and is constructed in "frequency domain" [36,37]. In this approach, excited state properties are derived as a linear response to an applied periodic perturbation. The

system response is described by means of a kernel K, which in the adiabatic approximation includes the Coulomb interaction and a local correction due to exchange and correlation [33,36,37]:

$$K_{ij\sigma,kl\tau} = \iint \phi_{i\sigma}^*(\vec{r})\phi_{j\sigma}^*(\vec{r}')\left(\frac{1}{|\vec{r}-\vec{r}'|} + \frac{\delta v_\sigma^{xc}(\vec{r})}{\delta\rho(\vec{r}')}\right)\phi_{k\tau}(\vec{r}')\phi_{l\tau}(\vec{r}')d\vec{r}\,d\vec{r}' \qquad (8)$$

where the orbital indices and spin are given by (i, σ), and v_σ^{xc} is the exchange-correlation potential. Within this approach the transition energies, Ω_n, are obtained from an eigenvalue problem involving the operator K and the Kohn-Sham excitation energies.

$$\left[\omega_{ij\sigma}^2\delta_{ik}\delta_{jl}\delta_{\sigma\tau} + 2\sqrt{f_{ij\sigma}\omega_{ij\sigma}}\,K_{ij\sigma,kl\tau}^{TDLDA}\,\sqrt{f_{kl\tau}\omega_{kl\tau}}\right]F_n = \Omega_n^2 F_n \qquad (9)$$

where $\omega_{ij\sigma}$ is the Kohn-Sham transition energies, and $f_{ij\sigma}$ are the differences between the occupation numbers of the i and j states. The eigenvectors F_n can be used to evaluate the oscillator strength for the transition, n. In either the real time description or the linear response regime, TDLDA can be regarded as a straightforward "add-on" to existing electronic structure code.

Both TDLDA approaches have strengths, which can be exploited depending on the nature of the problem. For example, the real time approach requires less memory and, in principle, it scales better for large systems than the linear response approach. Real time methods can also be used for nonlinear phenomena [34]. In contrast, linear response methods are much more efficient for "smaller systems" (less than a thousand eigenvalues or so) because the scaling prefactor is much smaller than in real time. Also, linear response or frequency domain methods can easily be used to exploit parallel computing platforms [41].

If the accuracy and ease of implementation of TDLDA can be extended to excited state properties, we will be able to obtain a successful series of applications and advances in fundamental knowledge of the excited state. Given the reduced computational load, TDLDA would likely be *the* method of choice for both excited and ground state properties. Initial applications of TDLDA include atoms, molecules, clusters and nanocrystalline matter (e.g., quantum dots) [33-40]. Comparisons with both experiment and more rigorous methods are quite promising.

A central activity of density functional approaches is to test and develop new functionals and to compare our results to other methods such as the GW-Bethe Salpeter approach as outlined in the previous section. Recent work has shown that hydbrid schemes and methods that attempt to include exact exchange functionals may improve predictions of excitation spectra and offer the opportunity to explore more exotic systems such as highly correlated systems [48-51]. Another outstanding problem is the accuracy of TDLDA for extended system. Recent progress in this area has been made using an exact exchange approach within time-dependent density-functional theory [52]. This procedure has yet to be applied to nanoscale structures.

3.2.D. Multi-level, multi-scale methods.

We plan also to solve the electronic structure and optical excitation of nanostructures using physically based multi-level, multi-scale methods. The goal is to extend the accurate methods described in the previous sections 3.2.A-C to nanosystems with thousands of atoms, while maintaining their accuracy as far as possible. There are three major approaches that we shall investigate. The first is an embedding method, which solves the electronic structure of an active region using accurate many-body methods, while representing the effects of its surrounding via a mean field embedding potential. The second approach is a patching scheme, which uses a divide-and-conquer strategy to construct the Hamiltonian of an entire nanosystem nonselfconsistently, and then solves the Hamiltonian of the whole nanosystem for only a few eigenstates relevant to its excited states. This method can extend the LDA and GW methods to still larger systems. The third approach is an orbital free method which can be used to study metallic nanocrystals, including its optical response and atomic relaxations.

The embedding method. In this method [53], the influence of the background (Region II) on the local region of interest (Region I) is brought in via an embedding potential calculated within DFT, that is added as a one-electron operator to the electronic structure calculations in region I. The embedding potential is based on orbital-free density functional theory (see the last part of this section for further details). We demonstrated the validity of this particular choice of embedding potential for metals, especially when gradient corrected functional are used. The $v_{embed}(r)$ is calculated self-consistently between regions I and II, while the whole system (I+II) is calculated via DFT and region I is calculated via an accurate many-body method. This has previously been done by us with many-body perturbation theory (MP2-4) using the HF molecular orbitals (MO's) obtained in the presence of the embedding potential. Configuration interaction (CI) and complete active space (CAS) methods have also been used for the active space. *We propose to extend the embedding theory to higher level methods such as multireference configuration interaction and coupled cluster theory (in combination with local correlation modeling as discussed earlier) in order to carry out very accurate calculations of excited states on metal surfaces and nanostructures [54]. We will work with applied mathematicians to enhance numerical stability through optimal choices of preconditioners .*

The patching method. The idea of the patching method is to construct the Hamiltonian based on a divide-and-conquer approach. This is feasible by realizing that many physical properties are short ranged spatially (Kohn's near-sightedness principle). For example, without a long range external electric field, the charge density at a given point will only depend on the local atomic environment at that point. Thus, a self-consistent calculation of a small system that contains the same local atomic environment will provide an accurate charge density in that region. We will carry out piece-wise self-consistent calculations, and then patch the physical properties together to yield the Hamiltonian of a large system. The first type of Hamiltonian we like to construct is the LDA Hamiltonian as discussed in Sec.3.2.C. Although LDA has a band gap error for the excited states, this can be corrected empirically by modifying the s, p, d pseudopotentials in a plane wave calculation [55]. To construct a LDA Hamiltonian, all one needs is the charge density of the system. We have developed a scheme [55,56,57] which generates charge motifs belonging to each atom, and then reassembles these motifs for a given nanosystem to yield the total charge density. The motifs are calculated as:

$$m_\alpha(r - R_0) = \rho_{LDA}(r) \frac{w(|r - R_0|)}{\sum_R w(|r - R|)} \qquad (10)$$

here $w(r)$ is a decaying weight function, thus $w(|r - R_0|)/\sum_R w(|r - R_0|)$ is a partition function which divides space into small areas, $\rho_{LDA}(r)$ is the self-consistently calculated LDA charge density of some small prototype systems. Besides the motifs themselves, their derivatives $md_i^\alpha(r)$ with respect to the positions of the bonding atoms are also calculated. Then, the charge density for a given nanostructure is constructed by reassembling the motifs as:

$$\rho_{patch}(r) = \sum_R m_\alpha(r - R) + \sum_R \sum_{R1} md_i^\alpha(r - R)(R1 - R)_i$$

here R1 are the atomic positions of the bonding atoms of atom at R, and subscript *i* denotes the Cartesian coordinates of (R1-R). This simple procedure yields remarkably accurate results, for semiconductor alloys (GaAsN) [57], fullerenes (carbon nanotubes and bucky balls)[56] and isoelectronic impurities [55]. The charge density error is typically less than 1% compared to directly calculated values, and the resulting energy error is less than 50 meV. Notice that these errors are of the same order as the numerical error produced by a typical planewave basis set cutoff. For some systems, the motifs might not all correspond to each atom, but instead to larger active areas (e.g., an impurity [58], a nanowire connecting quantum dots, or an adsorbate on a nanosurface). Another challenge for the charge patching method is to deal with the long range electric field effect. To do this,

we propose to calculate the polarization of the charge motifs. As a result, the classical long range electrostatic problem can be solved self-consistently.

Our next step is to extend the above approach to other high accuracy methods, e.g., the GW method discussed in 3.2.B. The challenge here is to get information on $\sum(r,r',E)$ from prototype (e.g., bulk) calculations, and then transfer the information to model a nanostructure. The challenge here is to find a way to handle this nonlocal but relatively short range operator, and to transfer its information from the prototype system to the nanostructure. After the Hamiltonian H has been constructed, the next step is to solve the single particle eigen states ϕ_i from the single particle Schrödinger's equation. For most optical properties, only a few states near the band edge need to be calculated. This is an interior eigenvalue problem; currently we are using the folded spectrum method (FSM) [59] to solve it. In FSM, the original Schrödinger equation is replaced by $(H - E_{ref})^2 \phi_i = (E_i - E_{ref})^2 \phi_i$, where E_{ref} is a reference energy placed inside the energy gap. Since only a few end of spectrum states are solved, the problem scales as O(N). However, new algorithms are needed as one encounters larger systems and smaller band gaps (see Sec. 3.3).

The orbital free method. In the "orbital-free" approach, one solves the quantum mechanical problem directly from the electron density, bypassing the calculation of orbitals [60]. Two quantities in conventional Kohn-Sham DFT usually are evaluated with orbitals present: one is the kinetic energy and the other is the electron-ion energy, when so-called "nonlocal" pseudopotentials are employed. In an orbital-free approach, the kinetic energy is evaluated instead as a functional only of the density and "local" pseudopotentials that only depend on position, r, are employed. If one could construct accurate kinetic energy density functionals (KEDFs) and accurate local pseudopotentials, then this orbital-free method could be applied to the entire periodic table, greatly simplifying calculations of electronic behavior (the orbital-free DFT method scales as NlogN, where N is related to system size). Recently, we have made progress developing KEDFs [61] and local pseudopotentials, and have shown that this allows the accurate treatment of surfaces and bulk crystals, even ones under shear, tensile, and compressive stress, at least for simple (non-transition) metals. Local pseudopotentials with as high accuracy as nonlocal pseudopotentials [62] have been constructed. As a result, one can now isolate the errors in the KEDFs themselves and work to further their development so that nonmetallic systems can be treated as accurately as main group metals. This OF-DFT approach has been used to study systems with hundreds and thousands of atoms, in, e.g., nanoparticle arrays [60b] in order to predict metal-insulator transitions observed experimentally upon compression of the array. Ultimately, a time-dependent formulation of OFDFT will be sought, in order to calculate conductances through nanowires from first principles.

3.3 Mathematical Challenges

This section describes four areas that require advances both in the underlying mathematical theory and in algorithm development to be able to address the application of the physical approaches described in the previous Section 3.2 to nanostructures.

3.3.A. Numerical Linear Algebra.

Numerical linear algebra is central to electronic structure calculations. The Schrödinger equation, the starting point for all electron state calculations, is an eigenfunction problem and many advances in electronic structure calculations, particularly in density functional based approaches, have come from its solution using new iterative and direct eigenvalue solvers. The solution of large systems of linear equations also arises in many approaches to solving the Schrödinger equation such as the coupled-cluster approach. Future advances in scaling up our methods for excited state calculations will require the development of new scalable solvers adapted to the specialized linear algebra problems arising in this field.

In the coupled-cluster approach, the conversion of the residual into a new amplitude as defined in Step 4, involves the solution of an ill-conditioned linear system **Ft=r**. This has its origin in the eigenvalue spectrum of the coefficient matrix **F**, and thus requires development of suitable preconditioners, together with gradient search methods that are stable in the presence of this ill-conditioning. This same step will arise in the iterative solution of the eigenvalue problem for excited states. We propose to investigate new preconditioners for these types of problems in conjunction with new search methods possibly through using deflation techniques to address the ill-conditioning

Within the GW/BSE approach, the current calculation of optical properties relies on first calculating and then diagonalizing very large, dense Hermitian matrices. For a number of atoms N_a in the system, the size of the matrix is proportional to $N_a{}^2$, the calculation of the matrix scales as $N_a{}^6$, and diagonalization scales as $N_a{}^6$. At present we are using the parallel direct solver routines in SCALAPACK. However, we are often only interested in the eigenstates and energies of the lowest few states. Therefore, in this proposal we would like to investigate the use of iterative parallel solvers based on conjugate gradient techniques or Lanczos for this problem [63]. In addition, we believe that if we forgo storage of the Hamiltonian and use Fourier transformation techniques, we can work in representations where the Hamiltonian is quite sparse and thus apply the Hamiltonian to an arbitrary vector with an effort scaling only with $N_a{}^4$. Therefore, we will study the use of sparse iterative approaches to this problem. In addition to this we would like to study methods for directly calculating electronic properties of the system such as the density of states without explicitly calculating the eigenvalues and eigenstates (e.g. via the recursion method).

Another area that we will address is the development of numerical methods to extend TDLDA to large systems, i.e., systems of several thousand atoms, appropriate for exploring the nano-structured matter. With respect to real time approaches of TDLDA, the chief bottleneck is a poor prefactor owing to the small time step required to describe the wave function evolution [40]. We will explore several ways of improving this technique. For example, it is possible to exploit "groups" of wave functions, which can be integrated simultaneously. In addition, we will use exponential propagation based on Krylov subspace methods for developing integration schemes such as those discussed in Refs. 41-46. In this context, it will be interesting to explore "block methods" such as block-Arnoldi. These methods have had great success in solving linear systems with several right hand sides.

With respect to TDLDA codes that are based on a frequency domain approach, the evaluation of matrix elements is difficult and consumes most of the CPU time of current implementations. The use of parallel platforms can mitigate this issue, but the N^4 scaling of the method presents a fundamental computational challenge. The bottleneck for frequency domain calculations is centered on evaluating the kernel, K. The double integration is computationally intensive. However, it can be handled by solving a Poisson equation problem, for example through the use of multigrid approaches as outlined in [41], followed by a single integration. An alternative solution is to express $V_{ij\sigma}$ in terms of a plane wave basis.

Either real time or frequency domain approaches require an initial solution of the Kohn-Sham equations to determine the eigenvalues ($\omega_{ij\sigma}$) and eigenvectors ($\phi_{i\sigma}(\vec{r})$). There are a variety of codes available for this task, e.g., Gaussian or real space codes. Much of our prior work has focused on a real space implementation of this problem. Typically, we solve the Kohn-Sham problem on a uniform grid using a higher order finite difference method. We extract the required eigenpairs using a generalized Davidson iteration method. This method is easy to parallelize and has been used for systems exceeding 1,000 atoms [47]. Similarly to the GW/BSE eigenvalue problem we would like to explore other iterative solvers such as conjugate gradient to see if they are more efficient for our problem

For the interior eigenvalue problem within the patching method, we are currently using the folded spectrum method (FSM) [59]. The conventional shift and invert method cannot be used here since the matrix is too large to

be calculated. The problem with the FSM is that the condition number of $(H - E_{ref})^2$ is much worse than the original H. This is particularly true if the band gap is small. Recently, Tackett and di Ventra [64] have used a Jacobi-Davison method to solve this problem. This method is based on H itself rather than $(H - E_{ref})^2$. Although the initial results are encouraging, much more work needs to be done, especially to understand the convergence under different situations. We have also investigated various Lanczos methods on $(H - E_{ref})^2$ [63]. However there are several issues to be resolved for the Lanczos method including 1) how to use preconditioning, 2) how to use almost converged eigenvectors from previous calculations (e.g., from self-consistent outer loop iterations), and 3) investigating the stability of the methods. Although Lanczos methods are very popular in other areas such as engineering, it is rarely used [65] in electronic structure calculations due to these problems.

3.3.B. Optimization

The optimization challenges for nanoscience problems arise in two different contexts. At the heart of many of the physical approaches lies a large-scale energy minimization problem. Various techniques have been developed to solve these problems, but as the size of the systems become larger many of these techniques are slow to converge and can sometimes even fail. The second area where optimization is used is in model parameter identification. In this context, the challenge is in developing constrained optimization methods for data fitting that can handle uncertainty in the experimental data as well as the simulations.

Energy Minimization. As an example of the first type of optimization problem, the orbital update in of the calculation of the energy for the coupled-cluster approach is a challenging problem. Unlike the normal orbital optimization problem in mean-field calculations, the second derivative matrix does not appear to be diagonally dominant, and relatively large orbital displacements may be required. At the same time, this step will determine the overall cost of the calculation and thus development of an effective approach, perhaps based on more extensive use of second derivative information than usual may be productive.

A second example of minimization arises in the TDLDA approach when computing forces in the excited state. Nano-structured materials often exhibit a Franck-Condon shift, owing to a relaxation of the excited state structure. Determining this relaxation is difficult owing to the large number of atoms present and reduced symmetry of such systems. The use of accurate quantum derived forces allows one to use codes to minimize the energy of the excited state configuration. However, the forces must be determined in the presence of an electron-hole pair. Only a few formalisms provide for the solution of this problem. However, TDLDA can be used for this task, at least for the lowest energy configuration, where no level crossing occurs. One possible procedure is to determine excitation energy of the system, E_s, in state s relative to the ground state energy, E_o:

$$E_s = E_o + \Omega_s \qquad (11)$$

where Ω_s is the excitation energy as determined from TDLDA. One can take the derivative of this equation with respect to the atomic position, R:

$$\frac{\partial E_s}{\partial R} = \frac{\partial E_o}{\partial R} + \frac{\partial \Omega_s}{\partial R} \qquad (12)$$

The derivative of the ground state energy with position can be determined by using the Hellmann-Feynman theorem. The derivative of the second term can be calculated with knowledge of the eigenvectors in equation (8), i.e.,

13

$$\Omega_s^2 = F_n^+ \left[\omega_{ij\sigma}^2 \delta_{ik} \delta_{j\ell} \delta_{\sigma\tau} + 2\sqrt{f_{ij\sigma}\omega_{ij\sigma}} \, K_{ij\sigma,k\ell\tau}^{TDLDA} \sqrt{f_{k\ell\tau}\omega_{k\ell\tau}} \right] F_n \qquad (13)$$

The derivative of Ω_s can also be performed using perturbation theory. This formalism has not been implemented in our codes, but should be a straightforward procedure.

We propose to develop new nonlinear optimization methods for these energy minimization problems. Initially we will extend a class of methods (TRPDS) [66] that combine the parallel pattern search method and the trust-region method to these energy minimization problems. TRPDS has been shown to have rapid convergence rates typical of Newton type methods while gaining the advantage of parallelism inherent in the parallel direct search methods. These methods are best suited for small to medium scale optimization however, and need to be extended to the large-scale case for applicability to nanosystems. We propose to extend that earlier work through the addition of nonlinear interior point methods. These methods, originally proposed for linear programming problems, have been extremely successful in that domain. Additionally, we propose to investigate matrix-free methods using preconditioners based on physical considerations derived from the second order information available.

The developments described above, if successful, represent valuable advances in quantum chemistry methods to make them applicable to nanoscale problems. They will be extensible to permit treatment of higher correlations (triples, or three-electron correlations, in the coupled cluster instance). They will also be extensible to permit analytical evaluation of energy gradients since they build on analytically computable matrix elements.

Parameter Estimation. Another application of optimization arises in fitting a theoretical model to experiment. This "theory of the experiment" will rely on first-principles results of electronic structure and excitation calculations. In this case, we need to find the globally optimum theoretical parameters that explain the experimental observations. In these cases, the objective function has many local minima, which tend to become smaller in extent (closer together) and to acquire similar minimum values, as the structural complexity increases. Genetic algorithms and simulated annealing have been used in the past, but more effective approaches are highly desirable. In particular, there is a need for optimization methods that take uncertainty in both the experimental data as well as the simulation results into account.

The Advanced Light Source and the Molecular Foundry, both at LBNL, offer an interface to experiments that study nanostructures. Such nanoscale experiments often require advanced theory to extract the important structural, electronic, optical, magnetic, chemical and other information that lead to fundamental understanding and prediction. Experimental techniques to be modeled theoretically and computationally include:

- Scanning tunneling microscopy, atomic-force microscopy and magnetic-force.
- Photoemission for studying the valence electronic structure of low-dimensional structures.
- X-ray absorption fine structure (XAFS) for characterizing a variety of materials, particularly at solid/gas and solid/liquid interfaces.

To address this set of problems, we propose to develop methods for optimization under uncertainty and uncertainty quantification. In simple terms, the main goal of uncertainty quantification is to develop methods for computing the uncertainty in the simulation outputs as a result of uncertain inputs. These uncertainties can arise from both parameter and model uncertainties. Various approaches have been attempted to compute uncertainty, including perturbation techniques, Monte Carlo, and pattern searches. Many of these methods typically result in the computation of a large multi-dimensional integral, which can be computationally expensive. Several recent approaches have been proposed that could provide a computational breakthrough for these problems. The first approach involves the use of Bayesian statistics in conjunction with several new methods for the fast integration of the resulting multi-dimensional integrals. The second approach involves an idea originally due to Wiener that proposed the use of polynomial chaos expansions to represent the desired probability distribution functions. This approach, recently advocated by several groups, is similar to using a Fourier expansion except that the

representation of the unknown quantities is in terms of a polynomial that is a function of random variables. The resulting multi-dimensional integrals can then be reduced to products of easily computed one-dimensional integrals. A third approach involves using a procedure known as Proper Orthogonal Decomposition (POD) as means of computing a reduced order model. This decomposition can then be used to compute various measures of uncertainty such as sensitivities and main effects. This proposal seeks to investigate these approaches as alternatives to current methods for uncertainty quantification.

As part of the uncertainty quantification problem, we will also develop methods for model reduction and surrogate functions. The main idea is to develop techniques for constructing cheap surrogate functions that can be used in place of the more expensive simulations. We propose to investigate the use of a hierarchy of surrogate models of various degree of fidelity within a model management framework. Furthermore, both linear and non-linear constraints will be incorporated to take advantage of known experimental data to limit the search domain, and parallelism will be exploited.

3.3.C. Scalable Computational Kernels

In several of the physical approaches, bottlenecks involve the computation of quantities that are needed to set up either the linear or nonlinear equations. In these cases, what are required are scalable methods for the efficient evaluation of certain intermediate quantities, integrals, and matrix elements. This section describes three areas where new mathematical techniques could address several bottlenecks and extend the range of systems that can be investigated through the physical approaches.

Intermediate quantities. In the GW/BSE approach, the first step involves solving for energy eigenstates $\psi_n(r)$ and eigenvalues E_n of a system. We typically expand $\psi_n(r)$ by a Fourier expansion for the states with Fourier modes labeled by wave vectors G:

$$H\psi_n = E_n\psi_n \quad , \quad \psi_n(r) = \sum_G c_n(G) \exp(iG \cdot r)/\sqrt{V} . \qquad (14)$$

Here H is a Hermitian Hamiltonian, V is the volume of the system over which integrals in r are performed, $c_n(G)$ are complex-valued expansion coefficients, and the integer n labels a discrete eigenstate.

We are always interested in states with the lowest energies, so denote E_1 as the ground-state of H. The first n_v states are the "valence" states and must be calculated explicitly. The next B states are used as intermediary quantities below. Also denote the size of the basis set, the number of G vectors, by N_G. Typically, $n_v << B << N_G$, with a typical case being $n_v \sim 50, B \sim 1000,$, and $N_G \sim 30,000$. Applying the Hamiltonian to a vector scales as $n_v N_G$ and calculating the B lowest states scales as $B^2 N_G$.

To compute the electronic bands in the system, we must compute a series of functions based on $\psi_n(r)$ and E_n. Below, we list the generic form of these functions in r; however, in actual computations, we work in the wave vector (G) representation.

One quantity we need to compute is the polarizability P, given by

$$P(r,r') = \sum_{n=1}^{n_v} \sum_{m > n_v}^{B+n_v} \frac{\psi_n(r)^* \psi_m(r) \psi_m(r')^* \psi_n(r')}{E_n - E_m} . \qquad (15)$$

In principle, the correct answer is obtained for $B \to \infty$; in practice, we truncate the sum for some finite value of B which ensures desired convergence. Another quantity we must compute, with similar structure to the polarizability is "the Coulomb-hole correlation", σ, for a state j.

One of the major bottlenecks is these calculations is the large number, B, of eigenstates of H required (scaling as $B^2 N_G$). As can be seen from equation (15), these states are only needed as intermediate quantities. One proposed approach is to bypass the calculation of the intermediate states to improve efficiency. Equation (15) shows that we only need the Green-function like object L defined as:

$$ L(r, r', z) = \sum_{m > n_v}^{\infty} \frac{\psi_m(r) \psi_m(r')^*}{z - E_m} \qquad (16) $$

to calculate P and σ. More precisely, we would like to be able to apply L to a state ψ_n efficiently, working directly in the G basis rather than r space. Our goal will be to devise a new method for applying L to an arbitrary state that will allow us to skip the calculation of the B intermediate states without decreasing the speed of the calculations for quantities such as the polarizability and Coulomb-hole correlation.

Integrating singular functions. Often, we require the integral of a function f over a fixed range of wave vectors q (in one, two, or three dimensions). The function f can have singular behavior for $q \to 0$ either as $|q|^{-2}, |q|^{-1}$, or $\ln |q|$ ($|q|$ is the Euclidean length of q). Furthermore, in more than one-dimension, there can be a strong dependence on the direction in which q approaches the origin. Brute-force integration around the singular behavior requires the use of very dense grids in q which makes calculations difficult. Currently, various ad-hoc methods are used to deal with the singularities, with success in only certain cases. As part of this proposal, we will develop more robust and generalized methods of dealing with these singularities.

Interpolation of matrix elements. As we have seen in the section above on numerical linear algebra the computation of the eigenvalues of the Hamiltonian can be expensive. In other cases, the calculation of the matrix elements of the Hamiltonian can in and of itself be computationally expensive, particularly in solid-state systems where the eigenstates $\psi_n(r)$ are extended in r space. We have implemented an interpolation scheme, as described below, to deal with this problem in the GW/BSE approach. However, better interpolation schemes (or other novel schemes) are needed. If successful, these methods will lead to dramatic improvements in performance and the size of systems that can be dealt with. The technical issues and questions are briefly summarized below.

In extended solids the wavefunction is also summed over k vectors sampling the First Brillouin zone. The wave vector expansion of $\psi_{nk}(r)$ is modified from equation (14) by working with $u_{nk}(r)$ instead:

$$ u_{nk}(r) = \sum_G c_{nk}(G) \exp(iG \cdot r) / \sqrt{V} \qquad (17) $$

where the wave vectors G are such that $\exp(iG \cdot r)$ is periodic in the size of the simulation cell: if a is a vector which connects two periodically identical points in space, then $\exp(iG \cdot a) = 1$ for all G.

For optical calculations, we require matrix elements of various two-point functions $f(r,r')$ between the $u_{nk}(r)$ states. We have defined a two-point, periodic function $f_q(r,r')$ for use below. The typical Hamiltonian matrix element required is between products of pairs of $u_{nk}(r)$ states:

$$F_{lmk,npk'} = \int dr \int dr' u_{lk}(r)^* u_{nk'}(r) f_{k'-k}(r,r') u_{mk}(r') u_{pk'}(r')^* \qquad (18)$$

Unfortunately, the typical number of pairs of states required for accurate calculation is on the order of $10^3 - 10^4$ requiring the calculation of $10^6 - 10^8$ matrix elements $F_{lmk,npk'}$ in equation (18). The bottleneck comes from the requirement of many k and k' vectors in the sampling that makes the calculation intractable.

To overcome this bottleneck, we currently implement an interpolation scheme. The idea is to compute F on a coarse grid in the six-dimensional (k,k') space and then to interpolate to a finer grid when required. That is, we first calculate F using equation (18) on a coarse grid. Next, we compute "transfer matrices" $t_{nk}^{\tilde{n}\tilde{k}}$ which tell us how state $u_{nk}(r)$ is expressed in terms of states on the coarse grid. With these transfer matrices, we can rewrite the matrix elements of F in terms of the transfer matrices and $u_{nk}(r)$ defined on the coarse grid. This interpolation scheme reduces the density of the grid necessary to give accurate results. However, improvements in the interpolation scheme will be needed to reduce the number of coarse grid matrix elements that must be computed, which is the major computational burden of the entire process.

3.3.D. Multiresolution Methods

Although multi-scale mathematical techniques have potential application across a broad range of topics in nanoscience, we will focus on two specific initial target applications. The first application we will consider is developing techniques aimed at exploiting the locality of electron correlations in coupled cluster methods. Coupled cluster methods provide a systematic approach for introducing the effects of electron correlation into the Hartree-Fock approximation. Inclusion of these effects is necessary to obtain sufficient accuracy in the computed potential energy surfaces to predict chemical properties of the system. Unfortunately, traditional approaches to incorporating these correlation effects leads to very poor computational scaling, which limits the applicability of this approach to systems of roughly 20 atoms.

Electron correlation amplitudes are known to decay rapidly with separation. Recently, Head-Gordon and co-workers have begun developing methods aimed at exploiting this locality. Their approach, based on localizing correlations to individual atoms, represents the simplest local correlation model that is possible. Our goal is to pursue a more systematic mathematical approach to the electron correlation problem based on a generalization of the method of local corrections. The basic idea of this approach is to combine a highly accurate local solution with a global coarse representation of far-field effects that is inexpensive to compute. Smoothness and decay properties of the solution make the global coarse solution adequate for accurately representing effects of the far field on the local solution. The accuracy of the overall procedure is then governed by the location of the transition from the coarse to the fine solution.

To illustrate the idea more concretely, we consider the Coulomb interaction of classical particles. In this case, we want to solve

$$-\Delta \varphi = \sum_s q_s,$$

where φ is the field and the q's are the localized charges. We assume that we can obtain a local solution to the local problem

$$-\Delta \varphi^s = q_s$$

We also assume that we can define a coarse but computationally inexpensive representation of $-\Delta$ which we will denote by $-\Delta^C$. We now define a projection operator P and an interpolation operator I that transfer information to and from the coarse representation respectively. With these definitions, we can define

$$q_{eff} = -\sum_s \Delta^C(P\phi^s_{loc}),$$

where ϕ^s_{loc} is a local approximation to ϕ^s. We can then compute a representation of the far field by solving

$$-\Delta^C \varphi^C = q_{eff}.$$

We can now assemble the pieces of the solution to compute the solution

$$\varphi = I(\varphi^C - \sum_s P(\varphi^s_{loc})) + \sum_s \phi^s_{loc}.$$

This basic idea has been applied in several forms. Anderson's method of local correction uses a finite difference operator to represent the coarse grid solution. The fast multipole methods of Greengard and Rokhlin are based on series expansions to represent the coarse operator. Several issues must be addressed to apply this type of approach to the electron correlation problem. First, in the electron correlation setting there are additional, quantum mechanical forces such as exchange forces that must be included in addition to the Coulomb effects. Another issue is determining an appropriate representation for the coarse operator in the electron correlation setting. We note that a similar set of issues arise in evaluating the self-energy operator $\Sigma(r,r')$ in the GW + patching scheme. In particular, we need to find an efficient way to numerically carry out $\int \Sigma(r,r')\phi(r')d^3r'$.

The other application area we plan to address using multi-scale methodology is TDLDA. In this case our goal is to apply the optimal prediction methodology developed by Chorin and his co-workers to the time dependent Schrödinger equation

$$i\frac{\partial \phi_i}{\partial t} = H(t)\phi_i(t)$$

In conventional numerical methods, the basic idea is to include as many degrees of freedom as one can afford and solve a truncated system using those degrees of freedom. For many systems such as TDLDA, we cannot represent an adequate number of degrees of freedom for this truncation to be adequate. Of course, any effort to include the effect of these un-resolved degrees of freedom requires some additional information about the system. Optimal prediction is a methodology for incorporating information about the statistical behavior of un-resolved degrees of freedom to predict the dynamics of the system.

To make this notion more precise, imagine that we would like to solve the Schrödinger equation using n degrees of freedom; but we can only afford to compute with a much smaller number, m. However, we assume that we have a probability distribution that characterizes the statistical behavior of the unresolved degrees of freedom. If our goal is to predict the mean behavior of m variables, a reasonable way to recast the system is to approximate the right hand side in the Schrödinger equation by its conditional expectation with respect to the given probability measure given the current state of the m variables we are modeling. Within this framework, one can work out exact equations for the evolution of this conditional expectation. This evolution is expressed in terms of a generalized Langevin equation of the type found in statistical theories of irreversible phenomena. In particular, the evolution is of the form

$$\frac{\partial \hat{\phi}}{\partial t} = R(\hat{\phi}(t)) + \int K(\hat{\phi}(t-s))ds + F(t),$$

where $\hat{\phi}$ represents the resolve components of the simulation. In this form, R represents the Markovian component of the dynamics, the integral term represents memory effects in the system and F represents "noise" determined by an "orthogonal dynamics" equation. Although the Langevin equation gives a precise characterization of the dynamics, its evaluation is of the same computational complexity as the original system. Much of the literature on optimal prediction has focused on different approximations that avoid this computational complexity. In cases in which there is a clear separation of scales, the solution of the Langevin equation can be well approximated by the solution of a related, low dimensional stochastic differential equation.

Application of the optimal prediction methodology to TDLDA will involve a number of challenges. First, we must decide the best way to expand the Kohn-Sham orbitals in terms of a basis set. Nonstandard ways of expanding the solution may have better scale separation properties for modeling the dynamics. Second, we need to determine an appropriate probability measure for the un-resolved degrees of freedom.

Both of the research topics discussed above will require advances in both mathematical theory and computational methods. In both cases, key new ideas will be required. However, if we are successful in finding answers to some of these questions, there is a potential for making a substantial increment in the size of problems that can be treated.

4. Integration and Management Plan

This proposal is from the Lawrence Berkeley National Laboratory, with strong university links to UC Berkeley, UCLA, University of Minnesota, and New York University. It is built on a balanced team of applied mathematicians, theoretical scientists with expertise in extended, nanoscale, and molecular systems, and computational experts to help bridge the two areas.   Our co-principal investigators will be Martin Head-Gordon (Chemical Sciences, LBNL), and Juan Meza (Computational Research, LBNL). Other key personnel from the physical sciences are Emily Carter (UCLA, Director of Modeling and Simulation California NanoSystems Institute), James Chelikowsky (Chemical Engineering and Materials Sciences, Minnesota), Steven Louie (Materials Science, LBNL), and Michel Van Hove (Advanced Light Source, LBNL). On the mathematics side, additional team members include John Bell, Alexandre Chorin, Chao Yang (LBNL), Michael Overton (New York University), and Yousef Saad (University of Minnesota). Bridging these groups are Andrew Canning and Lin-Wang Wang (LBNL), with expertise in both algorithmic development and high-performance computing.

A critical aspect of this proposal will be the integration between application scientists and mathematicians to address the problems described in the proposal. Therefore, we have developed a management plan to help us achieve our goals. Our main strategy will be to organize the larger team around four smaller teams, each one of which will focus on one of the physical approaches described in Sections 3.2.A-D. Each team will consist of members from both the application sciences as well as members from the mathematical community. Together they will develop and be responsible for both a set of short and long-term goals. It is expected that there will be overlap between the team members as many of the mathematical challenges span more than one physical approach. In addition, we expect that new ideas developed within one sub-group may prove useful in other contexts and that cross-fertilization between the approaches will be beneficial. To enhance this cross-fertilization we will hold regular meetings, perhaps centered around a seminar series. The two lead principal investigators, Head-Gordon and Meza, will share the overall responsibility for assuring that the larger team goals are being met and that the sub-groups communicate with each other, for example through annual meetings for the entire team.

As an initial target, we have developed a set of goals to be accomplished within the first 18 months for each of the four main physical approaches, which we summarize below. In each case, we list the two people responsible for meeting the goals of each team, although we do not list everybody on the team.

Local Coupled-Cluster (Head-Gordon, Meza)
- Develop and test a local correlation approach for elementary excitations via coupled cluster theory, including efficient algorithms for solving associated ill-conditioned linear equations and eigenvalue problems.
- Develop an interface to a new optimization method based on an interior point strategy.

TDLDA (Chelikowsky, Saad)
- Implement a new time dependent density functional algorithm for examining the optical properties of nanoscale quantum dots with several thousand atoms.
- Investigate new functionals and hybrid methods that will be applicable to predict the properties of extended systems and highly correlated systems.

GW/BSE (Louie, Canning)
- Develop new methods and tool sets to enhance the capabilities and range of validity of the many-body Green's function approach.
- Combine this approach with other methods for large-scale applications.

Embedding and Patching Methods (Carter, Yang, Wang)

- Develop charge patching methods to calculate the surface of a nanostructure.
- Develop a new iterative algorithm for the interior eigenvalue problem.

These goals only encompass our short-term goals. The long-term goals are described in the full proposal and include such areas as the development of new computational scalable kernels, methods for optimization under uncertainty, and multiresolution techniques.

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Description of Facilities

LBNL's NERSC Division has established various computing and storages systems for research and development. Leading-edge computing platforms and services make NERSC the foremost resource for large-scale computation within DOE. An IBM RS/6000 SP makes up the heart of NERSC's computer hardware capability. NERSC's 3,328-processor IBM RS/6000 SP has 208 16-CPU POWER3+ SMP nodes with a peak performance of five teraflop/s, making it one of the most powerful unclassified supercomputer in the world. Each node has a common pool of between 16 and 64 gigabytes of memory, and the system has 20 terabytes of disk space. Additional capabilities are provided by two special-purpose servers: a cluster of four PCs for numerical and statistical processing, and a dedicated Silicon Graphics computer for scientific visualization from remote locations.

NERSC also has research activities in cluster architectures. The PC Cluster Project, is focused on two systems, on which we are developing the software infrastructure needed to use commodity hardware for high performance computing:

- the 36-node PC Cluster Project Testbed, which is available to NERSC users for trial use
- the 12-node Alpha "Babel" cluster, which is being used for Modular Virtual Interface Architecture (M-VIA) development and Berkeley Lab collaborations.

Access to NERSC from anywhere in the U.S. or the world is available through ESnet, which provides OC-12 bandwidth to NERSC and Argonne National Laboratory, T3 bandwidth on major backbone links, and T1 links over much of the rest of its coverage area.

In addition to the computational facilities, the nearby Advanced Light Source (ALS) and the planned Molecular Foundry will give the team access to experimental facilities. The Advanced Light Source (ALS), a division of LBNL, is a national user facility that generates intense light for scientific and technological research. As one of the world's brightest sources of ultraviolet and soft x-ray beams, and the world's first third-generation synchrotron light source in its energy range, the ALS makes previously impossible studies possible. The Molecular Foundry at Berkeley Lab, will open its doors on a limited scale in mid 2003 as an international user facility for the study of the theory, synthesis, and characterization of nanoscale materials. Full scale operations are expected to begin in 2006 when construction of its new building is complete. The focus of the Foundry will be on the development and understanding of both "soft" (biological and polymer) and "hard" (inorganic and microfabricated) nanostructured building blocks and their integration into complex functional assemblies.

Biographical Sketches

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Biographical information

Born March 17, 1962, in Canberra, Australia.
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Education

B. Sc. (1st class honours),	1983	Monash University, Melbourne, Australia
M. Sc. (thesis),	1985	Monash University, Melbourne, Australia
Theoretical chemistry,		*Professor Ronald D. Brown, supervisor*
Ph. D. ,	1989	Carnegie Mellon University, Pittsburgh, PA
Theoretical chemistry,		*Professor John A. Pople, supervisor*

Postdoctoral research

1989 - 1992: AT&T Bell Laboratories, Murray Hill, NJ
      Theoretical chemistry,   *Dr. John C. Tully, supervisor*

Professional experience

2000 – present	Professor of Chemistry, *University of California, Berkeley.*
1994 – present:	Faculty Chemist, *Lawrence Berkeley National Laboratory.*
1997 – 2000	Associate Professor of Chemistry, *University of California, Berkeley.*
1992 – 1997	Assistant Professor of Chemistry, *University of California, Berkeley*

Awards and honors

2001 – 2002	Miller Research Professor, Miller Institute for Basic Research in Science
2001	Departmental Teaching Award, Chemistry Dept, U.C. Berkeley
1998	Medal of the International Academy of Quantum Molecular Sciences
1995 – 2000	David and Lucile Packard Fellowship
1995 – 1997	Alfred P. Sloan Research Fellow
1994 – 1996	Hildebrand Chair in Chemistry
1993 – 1998	National Science Foundation Young Investigator Award

Professional activities

Over 150 scientific publications.
Over 120 invited lectures.
Editorial Advisory Board of Journal of Physical Chemistry
Editorial Advisory Board of Physical Chemistry Chemical Physics
Editorial Advisory Board of Journal of Theoretical and Computational Chemistry
Editorial Advisory Board of International Journal of Quantum Chemistry
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Biographical Sketch

Dr. Meza is the head of the High Performance Computing Research Department at Lawrence Berkeley National Laboratory. This department focuses on research in scientific data management, visualization, computational grids, numerical algorithms, and computational sciences and engineering. He is responsible for developing short- and long-term research and development plans and proposing new technology directions. Prior to joining Lawrence Berkeley National Laboratory, Dr. Meza held the position of Distinguished Member of the Technical Staff at Sandia National Laboratories and served as the manager of the Computational Sciences and Mathematics Research department. In this capacity, he acted as the Research Foundation Network Research program manager, the ASCI Problem Solving Environment Advanced Software Development Environment
program manager and served as a member of the Sandia California site Research Council.

Dr. Meza holds Ph.D. and M.S. degrees in Mathematical Sciences from Rice University. He also holds M.S. and B.S. degrees in Electrical Engineering (cum laude) from Rice University. His current research interests include nonlinear optimization and methods for uncertainty quantification, with a particular emphasis on parallel methods.   He has also worked on various scientific and engineering applications including molecular conformation problems, optimal design of chemical vapor deposition furnaces, thermal analysis, and semiconductor device modeling.

Recent Relevant Publications:

1) A Class of Trust Region Methods for Parallel Optimization, P.D. Hough, J.C. Meza, SIAM Journal of Optimization, Vol. 13, No.1, pp 264-282, 2002.
2) Can Data Recognize Its Parent Distribution? A.W. Marshall, J.C. Meza, I. Olkin, Journal of Computational and Graphical Statistics, Vol. 10, No. 3, 2001.
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5) A Multigrid Preconditioner for the Semiconductor Equations, J.C. Meza, R.S. Tuminaro, SIAM J. Sci. Comput.,Vol. 17, No.1, 118-132, 1996.

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Education: B.S. Chemistry (High Honors), UC Berkeley, 1982; Ph.D. Chemistry, Caltech, 1987

Professional Positions: Postdoctoral Research Associate 1987-88, CU Boulder; Assistant Professor (1988-92), Associate Professor (1992-94), and Professor of Chemistry, 1994-2002; Professor of Chemistry and Materials Science, 2002-, University of California, Los Angeles.

Selected Honors: NSF Presidential Young Investigator Award, 1988; Camille and Henry Dreyfus Foundation Distinguished New Faculty Award, 1988; Union Carbide Innovation Recognition Awards, 1989 & 1990; Camille and Henry Dreyfus Teacher-Scholar Award, 1992; Alfred P. Sloan Research Fellow, 1993; Exxon Faculty Fellowship in Solid State Chemistry, 1993; Medal of the International Academy of Quantum Molecular Sciences, 1993; Fellow of the American Vacuum Society, 1995; Peter Mark Memorial Award, American Vacuum Society, 1995; Dr. Lee Visiting Research Fellowship in the Sciences, Christ Church, Oxford University, 1996; Defense Science Study Group Member, 1996-97; Fellow of the American Physical Society, 1998; Visiting Scholar in Physics, Harvard University, 1999; Fellow of the American Association for the Advancement of Science, 2000; McDowell Lecturer, University of British Columbia, 2002; First Dean's Recognition Award for Scientific Research, UCLA, 2002.

Theoretical Chemistry: *Ab initio* energetics, kinetics, and dynamics of bulk and surface diffusion, reaction, and interface formation for semiconductors, metals and ceramics; multiscale modeling of the response of materials to chemical and mechanical stresses (e.g., hydrogen embrittlement and oxidation-induced cracking of metals); *ab initio* energetics and dynamics of combustion;development of new electron correlation, density functional , and simulation methods to bridge length scales.

Publication Highlights (out of 138)

E. A. Jarvis and E. A. Carter, "Importance of Open-Shell Effects in Adhesion at Metal-Ceramic Interfaces," *Phys. Rev. B*, **66**, 100103 (2002).

T. Kluener, N. Govind, Y. A. Wang, and E. A. Carter, "Prediction of Electronic Excited States of Adsorbates on Metal Surfaces from First Principles," *Phys. Rev. Lett.*, **86**, 5954 (2001).

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I. V. Ionova and E. A. Carter, "Ridge Method for Finding Saddle Points on Potential Energy Surfaces," *J. Chem. Phys.*, **98**, 6377 (1993).

E.A. Carter, G. Ciccotti, J.T. Hynes, and R. Kapral, "Constrained Reaction Coordinate Dynamics for the Simulation of Rare Events," *Chem. Phys. Lett.*, **156**, 472 (1989).

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Jim Chelikowsky obtained a BS degree, Summa Cum Laude, in physics from Kansas State University in 1970 and a PhD degree in physics from the University of California at Berkeley in 1975, where he held a National Science Foundation fellowship. He performed postdoctoral work at Bell Laboratories from 1976-1978 and was an assistant professor at the University of Oregon from 1978-1980. From 1980-1987 he worked at Exxon Research and Engineering Corporate Research Science Laboratories. In this capacity, he served as group head in theoretical physics and chemistry. He went to the University of Minnesota in 1987 as a professor within the Department of Chemical Engineering and Materials Science. He was named an Institute of Technology Distinguished Professor at Minnesota in 2001. He is also a Fellow at the Minnesota Supercomputing Institute.

He has been active within the Materials Research Society having organized several symposia and within in the American Physical Society where he served on the Executive Committee of the Division of Materials Physics from 1993-1996 and is currently the Chair of the Division. He was named a Fellow of the American Physical Society in 1987. He was awarded a John Simon Guggenheim Fellowship in 1996. During the tenure of this Fellowship he spent a sabbatical at EPFL, Lausanne, Switzerland. He was the Neal Amundson Professor of Chemical Engineering and Materials Science in 1996 and a Miller Institute Professor at the University of California at Berkeley in 1999. He received the David Turnbull Lectureship Award from the Materials Research Society in 2001.

His research has made significant contributions within the field of computational materials science.   His work has focused on the optical and dielectric properties of semiconductors, surface and interfacial phenomena in solids, point and extended defects in electronic materials, pressure induced amorphization in silicates and disordered systems, clusters and confined systems, diffusion and microstructure of liquids, and the development of high performance algorithms to predict the properties of materials. He has published over 240 papers, including 5 monographs.

Recent Relevant Publications:

1. I. Vasiliev, S. Ogut, and J.R. Chelikowsky: "Ab Initio Optical Absorption and Electronic Excitations in Hydrogenated Silicon Quantum Dots," Phys. Rev. Lett. **86**, 1813 (2001).
2. I. Vasiliev, R. M. Martin and J.R. Chelikowsky: "Effect of Surface Oxidation on the Optical Properties of Silicon Nanocrystals," Phys. Rev. B **65**, 121302 (2002).
3. L. Kronik, R. Fromherz, E. Ko, G. Gantefor, and J. R. Chelikowsky: "Electron Affinity and Metastability of Hydrogenated Silicon Clusters," Nature: Materials **1**, 49 (2002).
4. I. Vasiliev, S. Ogut, and J. R. Chelikowsky: "First Principles Density Functional Calculations for Optical Spectra of Clusters and Nanocrystals," Phys. Rev. B **65**, 115416 (2002).
5. J.R. Chelikowsky: "The Pseudopotential-Density Functional Method (PDFM) Applied to Nanostructures," J. Phys. D **33**, R33 (2000).

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Biographical Sketch

Professor Louie received his B.A. degree in physics and mathematics in 1972 and his Ph.D. in physics in 1976, both from the University of California at Berkeley. He was a postdoctoral fellow at the IBM Watson Research Center from 1977-79, a visiting member of the technical staff at the AT&T Bell Laboratories in 1979, and Assistant Professor of Physics at the University of Pennsylvania in 1979-80. He returned to the University of California at Berkeley as Associate Professor in 1980 and has been Professor of Physics since 1984. He is concurrently a Senior Faculty Scientist in the Materials Sciences Division of the Lawrence Berkeley National Laboratory.

His research interests are in theoretical condensed matter physics and nanoscience covering the areas of: electronic and structural properties of crystals, surfaces, interfaces and clusters; quasiparticle and optical excitations in solids; electron correlation effects in bulk and reduced-dimensional systems; solid state NMR; fullerenes and nanotubes; nanodevices; superconductivity; and *ab initio* pseudopotential theory. He has published over 340 papers and co-edited two monographs.

He is an editor of the journal *Solid State Communications* and has served on numerous national/international committees, boards, and panels.

Awards and Honors

Professor Louie is a Fellow of the American Physical Society. He received a NSF Postdoctoral Fellowship (1977), a Sloan Fellowship (1980), a Guggenheim Fellowship (1989), and two Miller Research Professorships (1986 and 1995). He was Eminent Visiting Scholar at the University of Tokyo (1989) and Municipal Chair Professor at the J. Fourier University, Grenoble, France (1990). He was awarded the U.S. Department of Energy Award for Sustained Outstanding Research in Solid State Physics (1993), the Lawrence Berkeley National Laboratory Outstanding Performance Award (1995), the Aneesur Rahman Prize for Computational Physics of the American Physical Society (1996), and the Davisson-Germer Prize in Surface Physics of the American Physical Society (1999). He is identified by the ISI as one of the 100 most highly cited researchers in the field of physics and one of the 25 most highly cited authors in nanoscience.

Recent Relevant Publications

1. S. Ismail-Beigi and S. G. Louie, "Excited-state forces within a first-principles Green's function formalism," Phys. Rev. Lett. 90, 076401 (2003).
2. S. G. Louie, "Electronic Properties, Junctions, and Defects of Carbon Nanotubes," in *Carbon Nanotubes*, *Topics in Applied Physics* 80, eds. M. S. Dresselhaus, G. Dresselhaus, and P. Avouris (Springer-Verlag, Heidelberg, 2001), p. 113.
3. H. J. Choi, J. Ihm, S. G. Louie, and M. L. Cohen, "Defects, Quasibound States, and Quantum Conductance in Metallic Carbon Nanotubes," Phys. Rev. Lett. 84, 2917 (2000).
4. M. Rohlfing and S. G. Louie, "Excitonic Effects and the Optical Absorption Spectrum of Hydrogenated Si Clusters," Phys. Rev. Lett. 80, 3320 (1998).
5. S. Ogut, J. R. Chelikowsky, and S. G. Louie, "Quantum Confinement and Optical Gaps in Si Nanocrystals," Phys. Rev. Lett. 79, 1770 (1997).

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Education	• 1965-1969 Federal Institute of Technology (*Eidgenössische Technische Hochschule*, ETH), Zürich, Switzerland
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Honors	• *Predoctoral Fellowship* (Aspirant), FNRS (Belgium) - 1971-74
	• *Visiting Senior Scientist*, University of Wisconsin - 1986
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	• *Invited Professor*, University of Paris - 1994
	• *Fellow* of the American Vacuum Society - 1994
	• *Fellow* of the American Physical Society - 1994
	• *Invited Professor*, Technical University of Eindhoven - 1995
	• *Outstanding Performance Award*, LBNL - 1996
	• *Invited Professor*, Université Aix-Marseille - 1996
	• *Invited Professor*, University of Hong Kong - 1996
	• *Adjunct Professor*, University of California at Davis - 1998
	• *Dept of Energy Award for Outstanding Scientific Accomplishments in Materials Chemistry* - 1998

Appointments	• 1969-1970	*Philips Research Laboratories*, Eindhoven, The Netherlands - Research Assistant
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	• 1977-1978	*University of Munich*, Institute of Physical Chemistry, and Institute of Crystallography and Mineralogy - Postdoctoral Fellow
	• 1986	*University of Wisconsin*-Milwaukee - Visiting Senior Scientist
	• Fall 1990	*University of California*, Berkeley, Dept. of Materials Science and Mineral Engineering - Lecturer
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Biographical Sketch

Dr. Bell received his B.S. (1975) degree from the Massachusetts Institute of Technology and his M.S. (1977) and Ph.D. (1979) degrees from Cornell University, all in mathematics. He is currently a Senior Staff Scientist and Group Leader for the Center for Computational Sciences and Engineering at the Lawrence Berkeley National Laboratory. Prior to joining LBNL, he held positions at the Lawrence Livermore National Laboratory, Exxon Production Research and the Naval Surface Weapons Center.

Dr. Bell's research focuses on the development and analysis of numerical methods for partial differential equations arising in science and engineering. He has made contributions in the areas of finite difference methods, numerical methods for low mach number flows, adaptive mesh refinement, interface tracking and parallel computing. He has also applied numerical methods to problems from a broad range of scientific and engineering fields such as combustion, shock physics, seismology, flow in porous media and aerodynamics.

Recent Relevant Publications

J. B. Bell, M. S. Day, J. F. Grcar, W. G. Bessler, C. Shultz, P. Glarborg, and A. D. Jensen, "Detailed modeling and laser-induced fluorescence imaging of nitric oxide in an NH_3-seeded non-premixed methane/air flame," *Proc. Combust. Inst.*, 29, 2002.

J. B. Bell, M. S. Day, J. F. Grcar, and M. J. Lijewski, "Numerical simulation of premixed turbulent methane combustion," *Proc. Combust*, Inst. 29, 2002.

J. B. Bell, M. S. Day, A. S. Almgren, M. J. Lijewski, and C. A. Rendleman, "A parallel adaptive projection method for low Mach number flows," *Proceedings of the ICFD Conference on Numerical Methods for Fluid Dynamics,* University of Oxford, March 26-29, 2001.

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A. L. Garcia, J. B. Bell, W. Y. Crutchfield, B. J. Alder, "Adaptive Mesh and Algorithm Refinement," *J. Comput. Phys.*, 154: 134-155, 1999.

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1992   Visiting Professor, College de France
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1991-   Fellow of the American Academy of Arts and Sciences
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1999-2000 Faculty Research Lecturer, University of California, Berkeley
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PUBLICATIONS:
1. Scaling laws and vanishing viscosity limits in turbulence theory (with G.I. Barenblatt). Proc.
Symposia Appl. Math. AMS, 54, (1998), pp. 1-25.

2. Optimal prediction of underresolved dynamics (with A. Kast and R. Kupferman). Proc. Nat. Acad.
Sci. USA, 95, (1998), pp. 4094-4098.

3. New perspectives in turbulence: Scaling laws, asymptotics, and intermittency (with G.I. Barenblatt).
SIAM Review, 40, (1998), pp. 265-291.
4. Turbulence: An old challenge and new perspectives (with G.I. Barenblatt). Meccanica, 33, (1998), pp.
445-468.

5. New perspectives in turbulence. Quart. Appl. Math., 56, (1998), pp. 767-786.

6. Unresolved computation and optimal prediction (with A. Kast and R. Kupferman). Comm. Pure Appl. Math., 52, (1999), pp. 1231-1254.

7. One-sided polarization and renormalization flow in the Kosterlitz-Thouless phase transition (with R. Kupferman). SIAM J. Appl. Math., 59, (1999), pp. 1843-1866.

8. A new formulation of the near-equilibrium theory of turbulence (with G.I. Barenblatt). ESAIM Proceedings Vol. 7, A. Giovannini et al. (eds), http://www.emath.fr/Maths/Proc</A, (1999), pp. 22-35.

9. On the prediction of large-scale dynamics using unresolved computations (with A. Kast and R. Kupferman). Contemp. Math., 238, (1999), pp. 53-75.

10. Optimal prediction and the Mori-Zwanzig representation of irreversible processes (with O.H. Hald and R. Kupferman). Proc. Nat. Acad. Sci. USA, 97, (2000), pp. 2968-2973.

11. Self-similar intermediate structures in turbulent boundary layers at large Reynolds numbers (with G.I. Barenblatt and V.M. Prostokishin). J. Fluid Mech., 410, (2000), pp. 263-283.

12. The characteristic length scale of the intermediate structure in zero-pressure-gradient boundary layer flow (with G.I. Barenblatt and V.M. Prostokishin). Proc. Nat. Acad. Sci. USA, 97, (2000), pp. 3799-3802.

13. Optimal prediction for Hamiltonian partial differential equations (with R. Kupferman and D. Levy). J. Comput. Phys., 162, (2000), pp. 267-297.

14. Stochastic optimal prediction with application to averaged Euler equations (with J. Bell and W. Crutchfield). Proc. 7th Nat. Conf. Comput. Fluid Mech., C.A. Lin (ed), Pingtung, Taiwan, (2000), pp. 1-13.

15. Non-Markovian optimal prediction (with O.H. Hald and R. Kupferman). Monte-Carlo Meth. & Appl.,7, (2001), pp. 99-109.

16. A model of a turbulent boundary layer with a non-zero pressure gradient (with G.I. Barenblatt and V.M. Prostokishin). Proc. Nat. Acad. Sci. USA, 99, (2002), pp. 5772-5776.

17. Optimal prediction with memory (with O.H. Hald and R. Kupferman). Physica D, 166, (2002), pp. 239-257.

18. Conditional expectations and renormalization. Multiscale Modeling and Simulation, 1, (2003), pp. 105-118.

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1999 – 2000	Householder Fellow, Oak Ridge National Laboratories, Oak Ridge, TN
1998 – 1999	Applications Consultant, Advanced Technical Computing Center, NEC Systems Lab, Inc., The Woodlands, TX

Professional Societies:

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Awards & Honors:

1999 Householder Fellowship in Scientific Computing. Oak Ridge National Laboratory
1998 Ralph Budd Award for best engineering thesis. Rice University
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MICHAEL L. OVERTON

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University of British Columbia   Computer Science   B.Sc., 1974
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Academic Appointments

1999-present   Professor of Computer Science and Mathematics
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1985-1990   Associate Professor of Computer Science
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Professional Activities

Michael L. Overton presently serves on the editorial boards of SIAM Journal on Optimization, SIAM Journal on Matrix Analysis and Applications, IMA Journal of Numerical Analysis, SIAM Review and ESAIM Journal on Control, Optimization during the 1995-1999. He is an elected member of the SIAM Board of Trustees, and serves on the Scientific Advisory Board of the Fields Institute for Research in the Mathematical Science and the Board of Directors of the Canadian Math Society.

Book

Numerical Computing with IEEE Floating Point Arithmetic (SIAM, 2001) is a short book intended to bring the key ideas of the IEEE floating point standard to a broad audience, both students and computer professionals. It has received enthusiastic reviews in *Computing Reviews, SIAM and Mathematical Reviews*. A Spanish translation has been published by the Mexican Mathematical Society.

Recent Journal Publications

Articles coauthored by Michael L. Overton appeared in the following journals during the 2001, 2002, or 2003 (pending): *SIAM J. Scient. Comp., IMA J. Numer. Anal., SIAM J. Matrix Anal. Appl., Linear Algebra and its Applications, Math. Operations Research, Foundations of Comp. Math., Proc. Amer. Math. Soc., SIAM J. Control Optim. And Math.Programming.*

Recent Graduate and Postdoctoral Advisees

M.V. Nayakkankuppam (PhD., 1999, now at University of Maryland, Baltimore County), F. Oustry (postdoctoral associate, 1998, now at INRIA, France)

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Biographical Sketch

Lin-Wang Wang received his PhD degree in physics from Cornell University in 1991. He was a Post-Doctoral Fellow under Alex Zunger at National Renewable Energy Laboratory (NREL) at Golden CO from 1992-1995, then a staff scientist in Biosym/Molecular Simulations Inc. in San Diego, CA. For 1996-1999, he moved back to NREL and became a senior staff scientist there. In 1999, he moved to LBNL. He has 15 year's of experience in large-scale electronic structure calculations. With his thesis advisor Michael P. Teter, he invented the Wang-Teter kinetic energy functional, now used in light metal (e.g., aluminum) total energy calculations without the Kohn-Sham orbitals. He has worked in O(N) electronic structure calculations in early 1990s. He has extensive experience in algorithm development and large-scale scientific computation. Worked with Alex Zunger, he invented the folded spectrum method, which pushed the limit of nonselfconsistent electronic structure calculations from 100 atoms to near a million atoms. He developed a linear combination of bulk bands (LCBB) method for semiconductor heterostructrure electronic structure calculations. This method makes empirical pseudo potential million atom calculations a routine in current research. He developed generalized moments method, which calculates the density of state and optical absorption spectra of a given system without explicit calculation of its eigenstates. He has used non-orthogonal Lanczos method for thousand atom systems. He also developed a popular parallel total energy plane wave pseudo potential program (PEtot), which is available to DOE community. He has studied Si quantum dots, CdSe quantum dots, InAs/GaAs embedded quantum dots, semiconductor alloys, isoelectronic impurity states in semiconductors, metallic alloys and precipitations, and metallic nanostructures. He is the author of about 70 peer-reviewed publications.

Andrew Canning, Computational Research Division, LBNL, acanning@lbl.gov

Andrew Canning is a staff scientist in the Computational Research Division (CRD) at the Lawrence Berkeley National Laboratory. He received his PhD in computational physics from the Physics Dept. Edinburgh University in 1988. He worked as a postdoc in Geneva University in the group of Prof. Enz (88-93) before moving to IRRMA at the EPFL (Swiss Federal college) Lausanne to work in the group of Prof. Car (joint originator of the Car-Parrinello method) (93-97). Position jointly paid for by Cray Research Inc. He then moved to the Lawrence Berkeley National Laboratory to work in the Scientific Computing group at the National Energy Research Scientific Computing Center (NERSC) (97-02). Andrew's main area of work has been in computational materials science particularly on the algorithmic and computing side. He is a joint developer of many codes used by the materials science community such as the code PARATEC (developed with Prof. Cohen and Prof. Louie's groups at LBNL, UCB) and ESCAN (developed with Lin-Wang Wang and Alex Zunger NREL) and used for electronic structure calculations for large nanostructures. He was one of the pioneers in introducing parallel computing into the materials science community, developing many new algorithms for parallelizing codes allowing new physics to be done on larger and more complex systems such as large nanostructures. He has also studied different types of eigensolvers such as Lanczos and Grassman approach for solving the Schrodinger equation which is central to all electronic structure calculations. He has gained awards for his work such as the Gordon Bell prize (1998), Smithsonian Laureate, (Computerworld, 2000), Gordon Bell prize (honorable mention, 2001). He has published over 40 papers in both physics as well as computational journals and has been invited to give talks at many conferences such as the March meeting of the American Physical Society.

Selected papers:

1 Parallel Empirical Pseudopotential Electronic Structure Calculations for Million Atom Systems. ,A. Canning, L.W. Wang, A Williamson and A. Zunger, Journal of Computational Physics, 160, p29 (2000)

2 Thomas-Fermi charge mixing for obtaining self-consistency in density functional calculations, D. Raczkowski, A. Canning and L.W. Wang, Phys. Rev. B. Vol 64, 12110(R) (2001)

3 Parallelization of the FLAPW Method, A. Canning, W. Mannstadt and A.J. Freeman, Computer Physics Communications, 130, p233 (2000).

4 Thick-restart Lanczos Method for Electronic Structure Calculations , K. Wu, A. Canning, H.D. Simon and L. W Wang, Journal of Computational Physics, 154, 156 (1999).

5 High Performance First Principles Method for Complex Magnetic Properties , B. Ujfalussy, X. Wang, X. Zhang, D.M.C. Nicholson, W.A. Shelton, G.M. Stocks, A. Canning, Y. Wang and B.L. Gyorffy. Gordon Bell Prize at SC98 Orlando. Proc. of SC98, Orlando, Florida, (1998).

6 Prediction of a Strain-induced Conduction-band Minimum in Embedded Quantum Dots, A.J. Williamson, A. Zunger and A. Canning, Phys. Rev. B, Vol 57, 8, R4253 (1998)

7 A Microscopic Model for Surface-induced Diamond to Graphite Transitions , A. De Vita, G. Galli, A. Canning and R. Car, Nature V379, N6565, 523 (1996).

8 Extended Si (311) Defects, J. Kim, J.W. Wilkins, F.S. Kahn and A. Canning, Phys. Rev. B, Vol 55, 24 p16186 (1997).

9 Structure and energy of the 90 degree partial dislocation in diamond: a combined ab initio and elastic theory analysis. , X. Blase, K. Lin, A. Canning, S.G. Louie, D.C. Chrzan. Phys. Rev. Lett. 84, p5780 (2000)

Appendix A: Nanoscience Glossary

Because some of the terminology may not be familiar to reviewers outside of their respective fields, we have compiled a short glossary of some of the most important terms within the computational chemistry and mathematics fields.

AO (Atomic Orbital) – A set of one-particle basis functions used in electronic structure calculations to expand the many-body wavefunction.

CC (Coupled Cluster) – A many-body theory in which the wavefunction is expressed as the exponential of a correlations operator acting on a mean-field reference function.

CCSD (Singles and doubles Coupled Cluster) – Coupled cluster theory in which the correlation operator is restricted to only single and double excitations.

CI (Configuration Interaction) – A many-body wavefunction that consists of a linear superposition of determinants.

correlation enery – Difference between the exact Schrodinger energy in a given single particle basis and the mean field Hartree-Fock energy.

DFT (Density Functional Theory) – An alternative to wavefunction-based theory in which the energy is expressed either fully or partially (in Kohn-Sham theory) as a functional of the electron density. Theorems due to Hohenberg and Kohn, and Kohn and Sham state that this is possible in principle.

exchange energy – A contribution to the total molecular energy rising from indistinguishability of electrons.

GGA (Generalized gradient approximation) – Improvements to the local density approximation, which allow an improved description of the slowly varying electron gas by including density gradients in the energy functionals.

Hartree-Fock Theory – The simplest approximate wavefunction-based theory of electronic structure, which is a mean-field approximation. The solutions are molecular orbitals, which are combined into a single determinant as the wavefunction.

KEDF (kinetic energy density functional) – A functional of the electron density that approximates the electronic kinetic energy. More commonly in Kohn-Sham DFT, the kinetic energy is obtained from a reference wavefunction, while other energy contributions are density functionals.

LDA (Local Density Approximation) - A method for describing the exchange-correlation energy of an electronic system as a function of the electron density

MO (Molecular Orbital) – The one-particle solutions of the Hartree-Fock equations. Excitation from occupied to virtual (empty) orbitals are often used to describe electron correlations.

TDDFT (Time Dependent DFT) – an extension of DFT to treat densities which are subject to time-dependent perturbations such as applied fields. Provides a basis for obtaining excited states from DFT calculations.